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GRANT # N00014-92-J-1629

R&T Code 4133037---01

Technical Report No. 10

Charge Transport and Water Molecular Motion in Variable Molecular Weight *NAFION* Membranes: High Pressure Electrical Conductivity and NMR

by

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Prepared for Publication in

Electrochimica Acta

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19950605 096

May 26, 1995

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REPORT DOCUMENTATION PAGE

Form Approved
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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	26 May 1995	Interim Technical Report

4. TITLE AND SUBTITLE
Charge Transport and Water Molecular Motion in Variable Molecular Weight NAFION Membranes: High Pressure Electrical Conductivity and NMR

5. FUNDING NUMBERS
Grant #
N00014-92-J-1629

R&T Code
4133037---01

6 AUTHOR(S)
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Hunter College of CUNY, Dept. of Physics
695 Park Avenue, NEw York, NY 10021

8. PERFORMING ORGANIZATION REPORT NUMBER
10

9 SPONSORING MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research, Physics and Chemistry Division
800 N. Quincy Street, Arlington, VA 22217-5660

10. SPONSORING MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
Accepted for Publication in Electrochimica Acta

12a DISTRIBUTION AVAILABILITY STATEMENT
Approve for public release; distribution unlimited

12b. DISTRIBUTION CODE

13 ABSTRACT (Maximum 200 words)

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14. SUBJECT TERMS
NAFION; Electrical Conductivity; NMR; High Pressure; Transport Mechanism; Activation Volume

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
unclassified	unclassified	unclassified	UL

Electrochim. Acta
(Newport)
(Corrected capture - Figs 7 & 8)

Charge Transport and Water Molecular Motion in Variable Molecular Weight *NAFION* Membranes: High Pressure Electrical Conductivity and NMR

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ABSTRACT

Measurements of the electrical conductivity and deuteron NMR spin-lattice relaxation times (T_1) in three different molecular weights of acid form NAFION conditioned at various levels of relative humidity have been carried out. Complex impedance studies were made along the plane of the film at frequencies from 10 to 10^8 Hz at room temperature and pressures up to 0.3 GPa. The NMR measurements were also made at room temperature and pressures up to 0.25 GPa. For all materials, the electrical conductivity decreases with increasing pressure. The calculated activation volume exhibits a large decrease (from 16 to 3 cm^3/mol) as the water content is increased from 2.4 Wt-% to 8 Wt-%. The activation volumes extracted from the NMR data show only a small further decrease as the water content is increased from 6 to 22 Wt-%. The activation volume dependence on water content represents further evidence that the transport mechanism in low water content materials is dominated by large scale segmental motions of the polymer chain, whereas at high water content the conductivity is more strongly influenced by the water than by the polymer. Finally, the data show that the electrical conductivity is smaller and the activation volume is larger for the higher molecular weight material.

Keywords: Nafion, Electrical Conductivity, Nuclear Magnetic Resonance, Transport Mechanism, Activation Volume, High Pressure

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INTRODUCTION

Because of their possible application in methanol fuel cells, the electrical conductivity of ion exchange membranes such as NAFION is of interest. While many studies of the electrical conductivity in these types of material have been carried out [1-11], very little work has been reported on the effect of molecular weight or high pressure on the conductivity. In a previous paper, the authors have presented some results for the effect of high pressure on the electrical conductivity and proton, deuteron and oxygen-17 NMR spin-lattice relaxation of NAFION 117 [12]. In the present paper, further measurements on NAFION 117 are reported along with measurements on other molecular weight materials. In addition, the ambient pressure electrical conductivity vs. water content is given for three different molecular weight materials.

EXPERIMENTAL DETAILS

All studies were carried out on NAFION 117 and 120 forms of NAFION manufactured by E. I. DuPont de Nemours and membrane C which was supplied by Los Alamos National Laboratory. Under dry conditions, the NAFION 117, 120 and membrane C samples are approximately 0.17, 0.26 and 0.145 mm thick, respectively and their respective repeat unit molecular weights are 1100, 1200 and 900.

For the electrical conductivity studies, strips of NAFION approximately 4 cm long and 1 cm wide were cut. Gold was vacuum evaporated onto the ends of the sample. The gold completely covered the ends of the sample (both sides and edges) leaving a strip of NAFION approximately 3 cm long and 1 cm wide. This

configuration has been shown to give good agreement with the bulk conductivity reported by other workers [4].

For the atmospheric pressure measurements, the samples were placed in sealed jars containing saturated solutions of various salts to control the relative humidity. The ends of the samples were connected to alligator clips attached to the ends of electrical feed-throughs which were epoxied into the lid of the jar. The NAFION 117 samples were pretreated as described previously [4]. The NAFION 120 and Membrane C samples were not pretreated (for NMR measurements, all membranes were pretreated). In each case the samples were dried over phosphorous pentoxide then successively conditioned at about 15, 25, 45, 70 and 100% relative humidities using saturated solutions as described above. The atmosphere in a glove box was also adjusted to each relative humidity using the saturated solutions and measurements of the dimensions and mass of the samples were carried out in the glove box. The Wt-% of water in the samples for the atmospheric pressure measurements was calculated by dividing the change in mass by the mass of the dry samples.

For the high pressure measurements, a sample was dropped directly from the lid of the controlled atmosphere jar into a jar of pressure fluid. The oily sample was then clamped onto the closure plug of the high pressure vessel used previously to measure the effect of high pressure on the electrical conductivity of ion conducting polymers [13]. The vessel was then closed and pressurized using a hydrocarbon pressure fluid, Spinesstic 38. A hydrocarbon pressure fluid was chosen because it is known that a similar material, teflon, swells much less when immersed in fluids which do not contain fluorine [14].

The equivalent parallel capacitance and resistance of the sample were then determined using both a CGA-83 Capacitance bridge (10-10^5 Hz) and a Hewlett Packard 4194A Impedance/Gain-Phase Analyzer. For the high pressure

measurements, the Impedance Probe was used with the Hewlett Packard instrument which has a frequency range of 10^4 - 10^8 Hz. All data were then transformed to the complex impedance, $Z^* = Z' - jZ''$.

For the NMR measurements, the samples were sealed in a rubber sheath immediately after determining their water (D_2O) uptake. Deuteron T_1's were measured by inversion recovery at a Larmor frequency of 29 MHz, using a high pressure probe described elsewhere [12]. Some effects of pressure history were observed, in particular a slight decrease in activation volume (up to about 25%) after one or two pressure cycles. For consistency, all T_1's reported correspond to the decreasing portion of the first cycle.

RESULTS

Electrical Conductivity vs. Water Content

Typical results for the electrical studies of NAFION are shown in Figure 1 in the form of complex impedance diagrams. In general, an impedance arc, attributable to the bulk properties of the material, is observed at the highest frequencies. In addition, a slanted line, due to blocking electrodes, is observed at the lowest frequencies. Because of the wide range of conductivity of the samples and different capabilities of the measuring instruments, different portions of the arc or line are observed for different samples at different water contents.

The data exhibit a slightly depressed semicircular arc, similar to that seen in ion conducting polymers for example [13]. This is consistent with the observation by various groups [4,11] that the electrical conductivity is attributable to a simple, frequency independent conductivity mechanism. In the present work, all intercepts due to semicircular arcs were obtained graphically assuming a symmetrical arc. The intercept of the impedance data with the Z' axis was

taken to be the bulk resistance, R, of the sample. The conductance, G=1/R, was then calculated from the intercept and transformed to the electrical conductivity, σ, via:

$$\sigma = G\ell/A. \qquad (1)$$

where A is the area of the sample and ℓ is the length.

The results for the variation of the electrical conductivity with water content are shown in Figures 2 and 3. (For a given type of NAFION, different samples were measured on the average at 3 relative humidities each.) The samples are indistinguishable when the conductivity data is plotted vs. Wt-% of water. However, when the electrical conductivity data are plotted vs. λ, which is the number of waters per sulfonate ion, as in Figure 4 it is clear that the electrical conductivity is highest for membrane C, particularly at the highest water contents. That is consistent with the results of Zawodzinski et al. [15].

In the course of the studies it was found that NAFION 120 has the least tendency to take up water. Specifically, if NAFION 120 is exposed to 100% relative humidity, it takes up only about 12-13 Wt-% of water by weight while NAFION 117 takes up about 28 Wt-% and membrane C takes up about 30 Wt-%. That is the reason that the electrical conductivity data for NAFION 120 do not extend to higher water contents. However, as will become apparent from the effect of pressure, the highest water content NAFION 120 samples behave similarly to the highest water content NAFION 117 and Membrane C samples.

Electrical Conductivity vs. Pressure

Because of the steps required for loading of the pressure vessel, it was possible that the water content of the sample could change during the process.

Consequently, the electrical conductivity of the sample while it was inside the pressure vessel was used to estimate the water content. The procedure was to calculate the electrical conductivity at approximately atmospheric pressure then determine the water content from the empirical line shown in Figure 3. Consequently, the water contents quoted relative to the pressure work represent indirect, albeit *in situ*, values.

In the case of the pressure measurements, arcs (from the Hewlett Packard 4194A) were frequently not obtained. In those cases and wherever possible, the low frequency data (from the CGA-83 capacitance bridge) were inspected for a region of constant conductance. In most cases, the data were relatively dispersion free for a decade on each side of 10^4 Hz. Further, the 10^4 Hz impedance data were very close to the intercept with the Z' axis. Consequently, in many cases the 10^4 Hz data were used to calculate the resistance and hence electrical conductivity for the pressure data. As will be shown, in cases where both types of data are used, there is relatively good agreement between the two types of data.

Next, because the bulk modulus or compressibility does not seem to be available for these materials, the approximation was made that the dimensions of the sample do not change upon application of pressure. Consequently, the geometrical factor (contained in equation (1)) obtained at atmospheric pressure was used at all pressures. Typical results for the variation of the electrical conductivity with pressure for low water content samples are shown in Figure 5. A slight positive curvature is observed. However, for all three molecular weights, when the water content was above about 10 Wt-%, different behavior was observed. Typical results for samples containing large amounts of water are shown in Figure 6. Strong negative curvature is observed. Because the reason for this behavior is not known, high pressure electrical conductivity data for samples

containing above 10 Wt-% of water will not be considered further in the present paper.

In all cases, a quadratic equation was fitted to the data and the initial slope was used to calculate an activation volume via:

$$\Delta V = -kT\,[d\ln\sigma/dp]_T. \qquad (2)$$

The results are given in Table 1 and are plotted in Figures 7 and 8. As discussed elsewhere [12] because of the omission of the compressibility, the activation volume is probably too large by on the order of 10%.

Deuteron NMR T_1 vs. Pressure

The activation volume for spin-lattice relaxation is given approximately by:

$$\Delta V = -kT\,[d\ln T_1/dp]_T. \qquad (3)$$

Previous work on NAFION 117 found good agreement between electrical conductivity and proton and deuteron activation volumes [12]. Because protons relax primarily through dipole-dipole interactions which are sensitive to translation, and deuterons relax primarily through nuclear quadrupole effects which are sensitive to rotation, the above agreement was taken as evidence that charge transport is correlated with molecular motion. Figure 9 displays variable pressure data for NAFION 120 with two different water contents, 20 Wt-% (λ = 12.0) and 6.8 Wt-% (λ = 4.1). The NMR activation volumes, listed in Table 2, are 2.9 and 4.0 cm^3/mol, for the higher and lower water contents, respectively. This trend is in agreement with that reported for NAFION 117 [12]. The effect of varying the molecular weight is shown in Figure 10. Results for NAFION 117

with 22 Wt-% (λ = 12.1) D_2O, NAFION 120 with 20 Wt-% (λ = 12.0) and Membrane C with 22 Wt-% (λ = 9.9), which are listed in Table 2, show that the activation volume decreases with decreasing molecular weight. The comparison between NAFION 117 and NAFION 120 is clear because their λ values are close; the argument for Membrane C is also reasonable because of its lower λ value, which tends to yield increased activation volumes.

DISCUSSION

For comparison with the electrical conductivity results, the NMR activation volumes have been included in Figures 7 and 8. There is good agreement between the two sets of measurements in the region of similar water contents. It will be of interest to extend the NMR measurements to lower water contents and the electrical conductivity measurements to higher and lower water contents. In fact, it would perhaps be more appropriate to examine proton NMR activation volumes at lower water content because even relatively isolated D_2O molecules can relax efficiently without contributing to charge transport. However, it is clear from the present results that the activation volume vs. water content curve exhibits two well-defined regions, one for $\lambda<5$ where the activation volume decreases rapidly with increasing water content and another for $\lambda>5$ where the activation volume is approximately constant at about 3 cm^3/mol. These two regions are correlated with the ability of NAFION to absorb water from the vapor phase [1]. Specifically, it is found that for $\lambda<5$ (region (i) of Zawodzinski et al. [1]) NAFION water uptake occurs very slowly with increasing water vapor activity. This is the region corresponding to solvation of the proton and sulfonate ions. For $\lambda>5$ (region (ii) of Zawodzinski et al. [1]), the polymer begins to swell.

The present results provide new information concerning these regions. For example, it is clear that fairly large values of the activation volume (up to 16 cm^3/mol) are observed for region (i). This is somewhat surprising for a proton conductor. These values found for the activation volume are typical of the values observed in the widely studied solvent-free polymer electrolytes [13]. This suggests that at low water content (region (i)) electrical transport is controlled by large scale segmental motions of the polymer chains. In the usual model of NAFION, there are "clusters" of water molecules and ions separated by polymer. The present result is consistent with such a model for low water content NAFION since in that case the electrical conductivity would be expected to be controlled by the amorphous polymeric region between the "clusters." In fact, it has already been shown [16] that in very dry NAFION the electrical conductivity exhibits VTF or WLF behavior which is also what is observed in typical solvent-free polymer electrolytes [12]. This interpretation is consistent with the work of Zawodzinski et al. [1] who have also concluded that ionic mobility in low water content membranes may be intimately tied with polymer motions.

For $\lambda>5$ (region (ii)), however, the activation volume is relatively small and varying the water content does not change the activation volume significantly. One interpretation is that the electrical conductivity in this region is controlled by more by the water than by the polymer. In fact, Zawodzinski et al. [1] have pointed out that since the water added in region (ii) swells the polymer i.e. fills the pores, the conductivity mechanism would be expected to approach that of bulk water. This would explain the present results since the activation volume for proton motion through water should be relatively independent of the amount of water.

Finally, it is apparent from Figure 8 and Tables 1 and 2 that the activation volume is somewhat larger for the higher molecular weight materials at a given number of waters per sulfonate group. In addition, it is apparent from Figure 4

that for higher water contents, at least, the electrical conductivity shows the opposite trend i.e. the higher molecular weight materials exhibit lower electrical conductivity.

For region (i), these results can be understood if the glass transition temperature for the higher molecular weight materials occurs at a higher temperature. The reason is that it is clear from work on solvent-free polymer electrolytes [13] that the activation volume *decreases* rapidly as temperature increases above the glass transition temperature. Consequently, since the highest molecular weight material has the largest activation volume, it would be expected to have the highest glass transition temperature. It is also clear from the work on solvent-free polymer electrolytes [13] that the electrical conductivity *increases* as temperature increases above the glass transition temperature. Consequently, since the highest molecular weight material has the smallest electrical conductivity, it would be again be expected to have the highest glass transition temperature. While no data appears to exist concerning the glass transition temperature, a higher glass transition temperature for a higher molecular weight is indeed a reasonable expectation.

The explanation of the results for region (ii) is not quite so straightforward. Even though the conductivity is more "bulk-like" it is clear that it is still affected by the polymer since the activation volume is largest and the conductivity is smallest for the highest molecular weight material. This is probably related to the density of sulfonate end groups and how they affect the polymer. Specifically, there are fewer sulfonates per volume for the largest molecular weight polymer. If a smaller density of end groups produces a smaller free volume, both results can be explained. First, the electrical conductivity will be certainly be smallest for the highest molecular weight material both because there are fewer ions per unit volume and because a smaller free volume should cause a smaller mobility of the

ions. Second, the activation volume results are explained because it and free volume have opposite effects. Specifically, smaller free volume results in a greater activation volume because the activation volume is the *change* in volume required for an ion to move. Consequently, a larger activation volume is expected for the higher molecular weight material because of the smaller density of end groups and correspondingly smaller free volume. Clearly, further work is necessary for a better understanding of these phenomena.

CONCLUSIONS

In summary, then, several results have been obtained via measurements of the electrical conductivity and deuteron NMR for different molecular weight NAFION at high pressure. For the lowest water content materials (about 2.4 Wt-%), the activation volume is quite large (about 16 cm^3/mol) and decreases rapidly as the water content increases. The activation volumes at low water contents represents further evidence that the transport mechanism in low water content materials is dominated by large scale segmental motions of the polymer chain. For high water contents (above about 8 Wt-%), as measured by NMR, the activation volume is on the order of 3 cm^3/mol and does not vary much with water content. This shows that the electrical conductivity at high water content is more "bulk-like." Finally, the activation volume is largest and the electrical conductivity is found to be smallest for the highest molecular weight material.

ACKNOWLEDGMENTS

This work was supported in part by the U.S. Office of Naval Research and the PSC-CUNY Research Awards Program. The authors would like to thank

Walther Grot of DuPont de Nemours for supplying the NAFION 120 samples and they are indebted to Dr. Thomas A. Zawodzinski, Jr. of Los Alamos National Laboratory for supplying the Membrane C samples.

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FIGURE CAPTIONS

Figure 1. Complex impedance diagrams at two pressures for membrane C containing 7.9 Wt-% (λ=3.9) of water.. The solid squares and circles represent datum points were obtained using a CGA-83 Capacitance bridge. The frequencies increase from right to left and the maximum frequency for that bridge is 10^5 Hz. The open squares and circles were obtained using a Hewlett Packard 4194A Impedance/Gain-Phase Analyzer. The frequencies are about 10^4 Hz to 10^8 Hz from right to left.

Figure 2. Electrical conductivity vs. water content in Wt-% for various samples of NAFION 120, Membrane C and NAFION 117 at room temperature (about 298 K).

Figure 3. Logarithmic plot of the electrical conductivity vs. water content in Wt-% for various samples of NAFION 120, Membrane C and NAFION 117 at room temperature (about 298 K).

Figure 4. Electrical conductivity vs. water content in λ, which is the number of waters per sulfonate, for various samples of NAFION 120, Membrane C and NAFION 117 at room temperature (about 298 K).

Figure 5. Electrical conductivity vs. pressure at room temperature (about 298 K) and various pressures for membrane C containing 4.9 Wt-% (λ=2.4) of water. The circles represent decreasing pressure and the triangle is increasing pressure. Also shown is the best-fit straight line. The data are the 10^4 Hz data from the CGA-83 capacitance bridge.

Figure 6. Electrical conductivity vs. pressure at room temperature (about 298 K) and various pressures for membrane C containing 14.8 Wt-% (λ=7.4) of water. The circles represent decreasing pressure and the triangle is increasing pressure. Also shown is the best-fit straight line. The data are the 10^4 Hz data from the CGA-83 capacitance bridge.

Figure 7. Activation volume vs. water content in Wt-% for various samples of NAFION 120, Membrane C and NAFION 117 at room temperature (about 298 K). The open symbols are calculated from electrical conductivity data and the solid symbols are from deuteron NMR data.

Figure 8. Activation volume vs. water content in λ, which is the number of waters per sulfonate, for various samples of NAFION 120, Membrane C and NAFION 117 at room temperature (about 298 K). The open symbols are calculated from electrical conductivity data and the solid symbols are from deuteron NMR data.

Figure 9. Pressure dependence of deuteron T_1 for NAFION 120 with λ = 12.0 (open circles) and λ = 4.1 (solid circles).

Figure 10. Pressure dependence of deuteron T_1 for NAFION 120 (λ = 12.0; open circles), NAFION 117 (λ = 12.1; solid circles) and Membrane C (λ = 9.9; triangles).

Table 1. Activation volume for various forms of NAFION conditioned at different relative humidities.

	Wt-% H_2O	λ	$\Delta V(cm^3/mol)$	
			10^4 Hz	HF Arc Intercept
Membrane C	4.9	2.4	7.5	
	7.9	3.9	3.2	2.4
NAFION 117	2.7	1.6	11.7	
	3.5	2.1	9.9	
	3.5	2.1	10.0	
	4.0	2.4	7.0	
	4.5	2.7	6.9**	
	5.6	3.4	5.3	
	5.6	3.4	5.3	5.6
	7.4	4.5	2.9**	
NAFION 120	2.4	1.6	16.1	
	2.8	1.9	14.9	
	4.1	2.7	7.6	
	4.2	2.8	7.5	
	6.9	4.6	2.5	3.0

**Reference 3.

Table 2: Activation volumes extracted from the deuteron T_1 pressure dependence. Measurements were made while decreasing the pressure.

		Activation Volumes (cm^3/mol)		
Wt-%	λ	Membrane-C	Nafion-117*	Nafion-120
22**	9.9	2.3±0.2		
22	12.1		2.6±0.2	
20	12.0			2.9±0.1
8**	3.6	4.2±0.1		
12	6.6		2.8±0.7	
6.8	4.1			4.0±0.1
6	3.3		4.6±0.2	

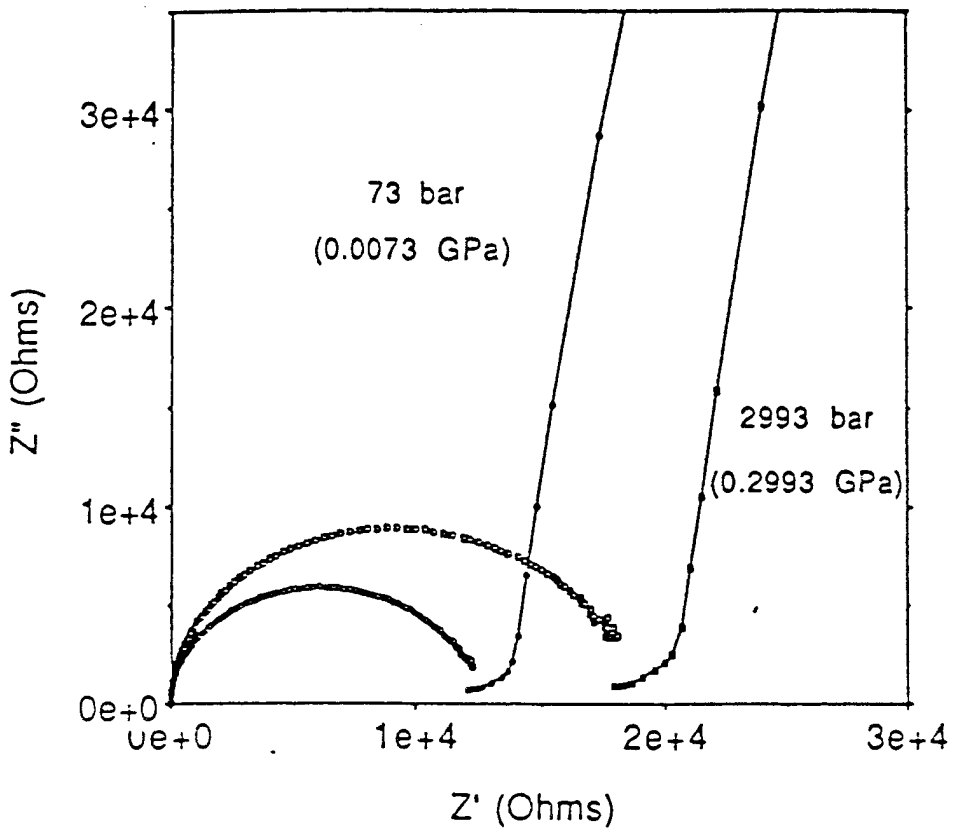
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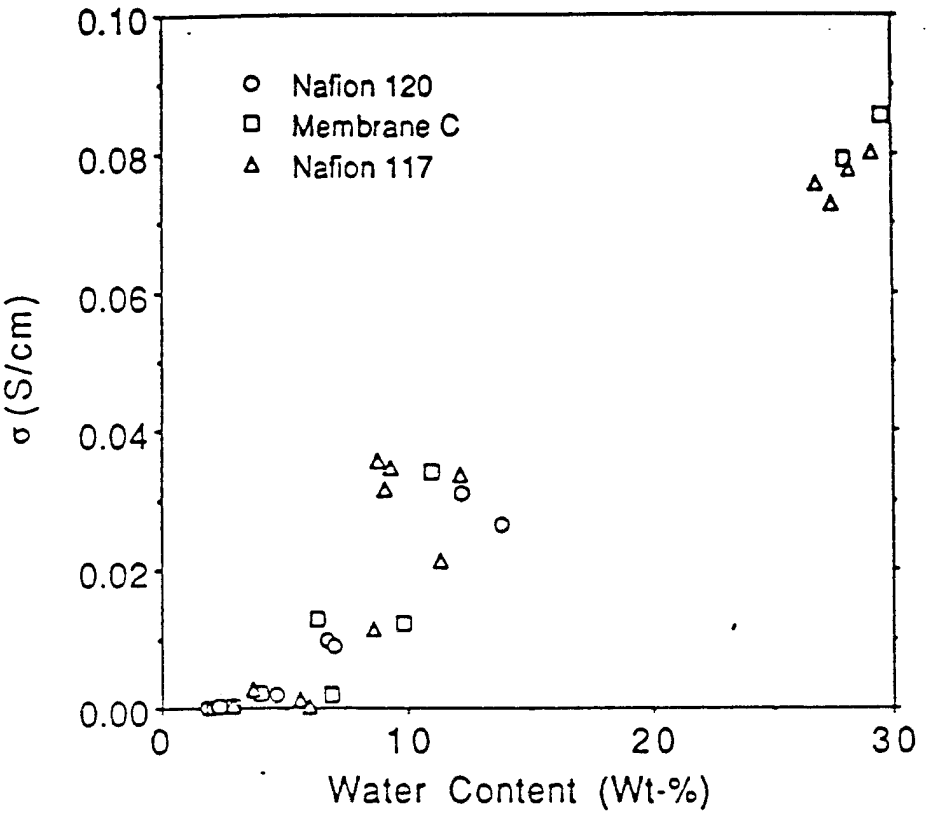
Fig 1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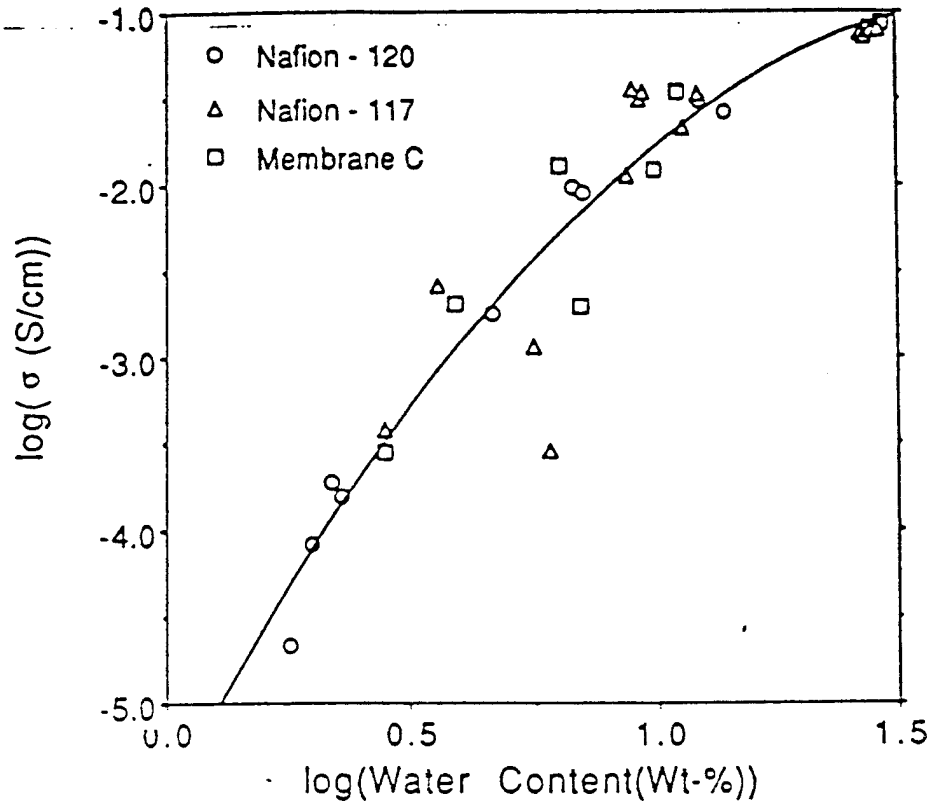
Water Content (Wt-%)

Figure 2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Nafion - 117
Membrane C
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-2.0
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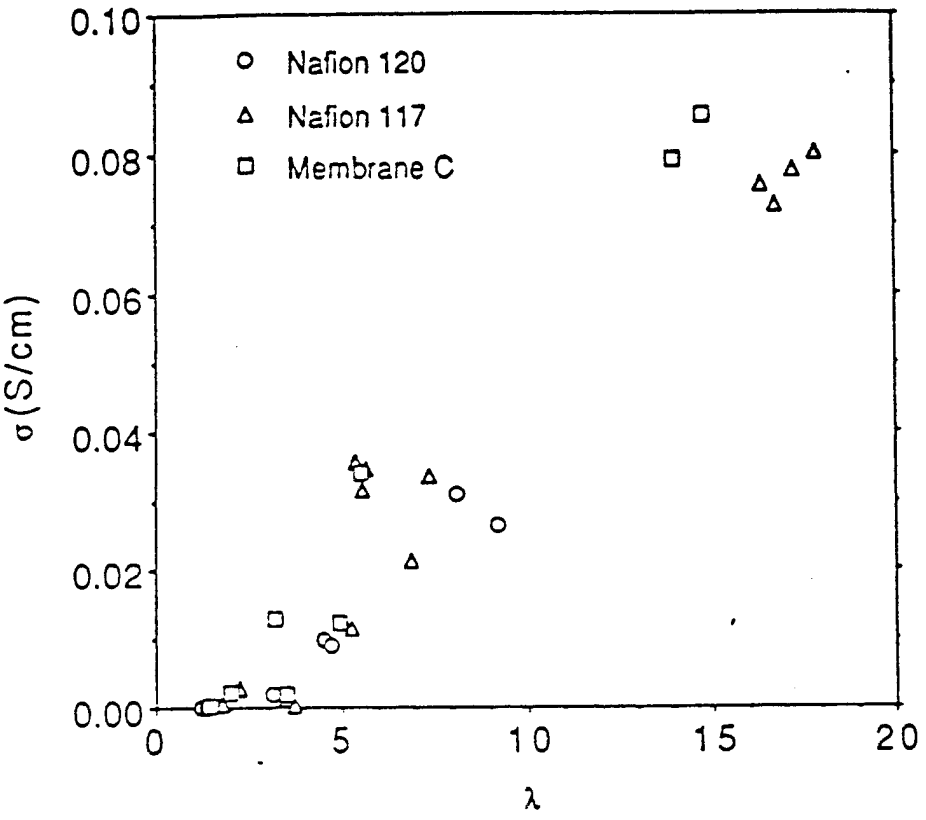
1.5
log(Water Content(Wt-%))

Figure 3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σ(S/cm)
Nafion 120
Nafion 117
Membrane C
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Figure 4

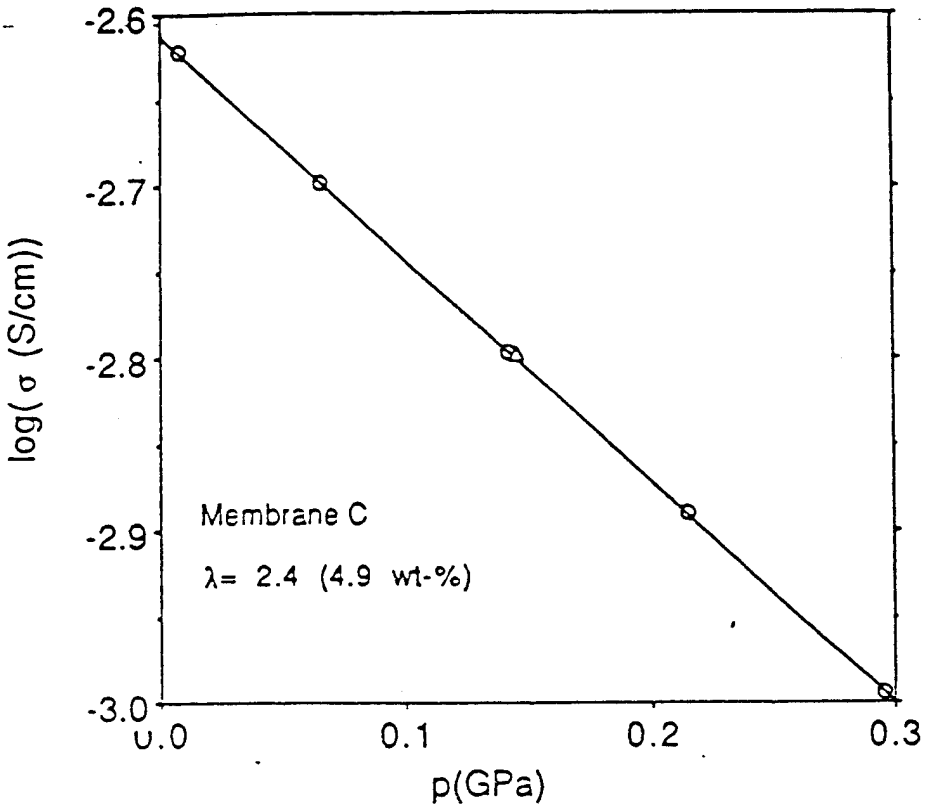


Figure 5

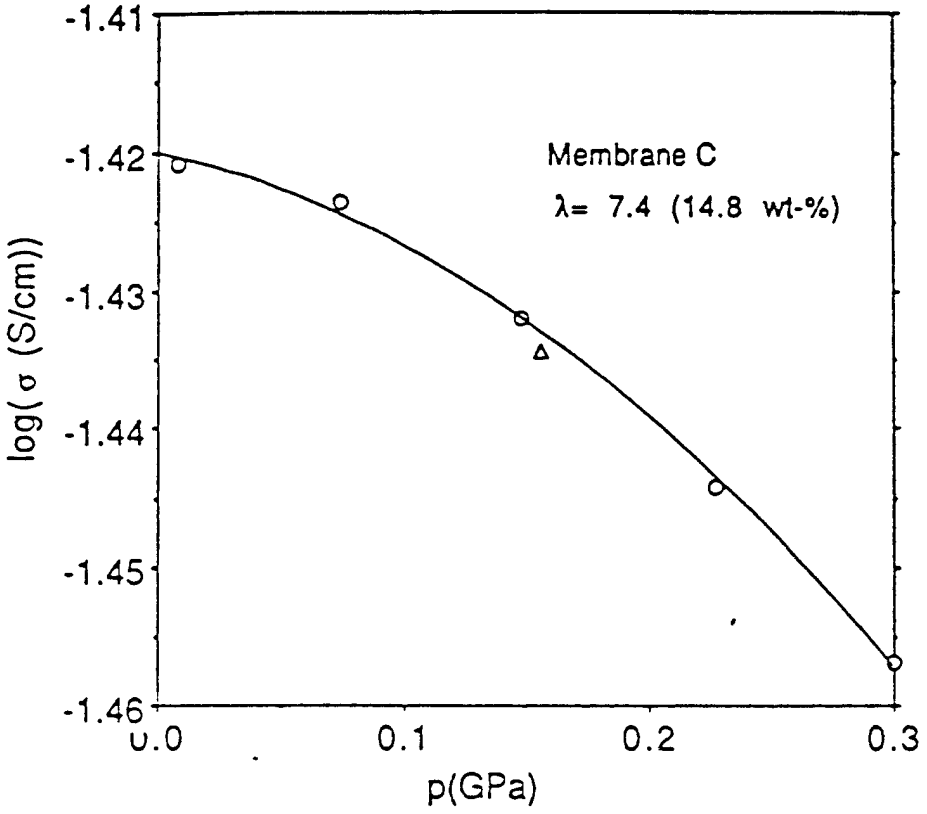

-1.41
-1.42
-1.43
-1.44
-1.45
-1.46
log(σ (S/cm))
Membrane C
λ= 7.4 (14.8 wt-%)
0.0
0.1
0.2
0.3
p(GPa)

Figure 6

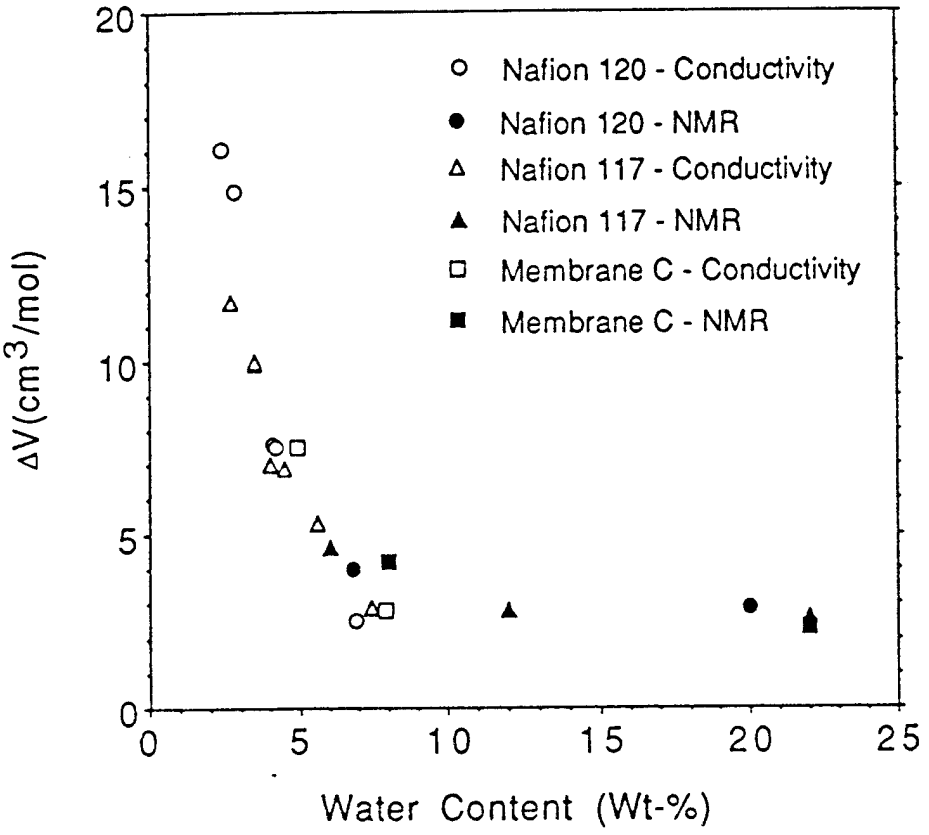

20
15
10
5
0
0
5
10
15
20
25
ΔV(cm3/mol)
Water Content (Wt-%)
Nafion 120 - Conductivity
Nafion 120 - NMR
Nafion 117 - Conductivity
Nafion 117 - NMR
Membrane C - Conductivity
Membrane C - NMR

Figure 7

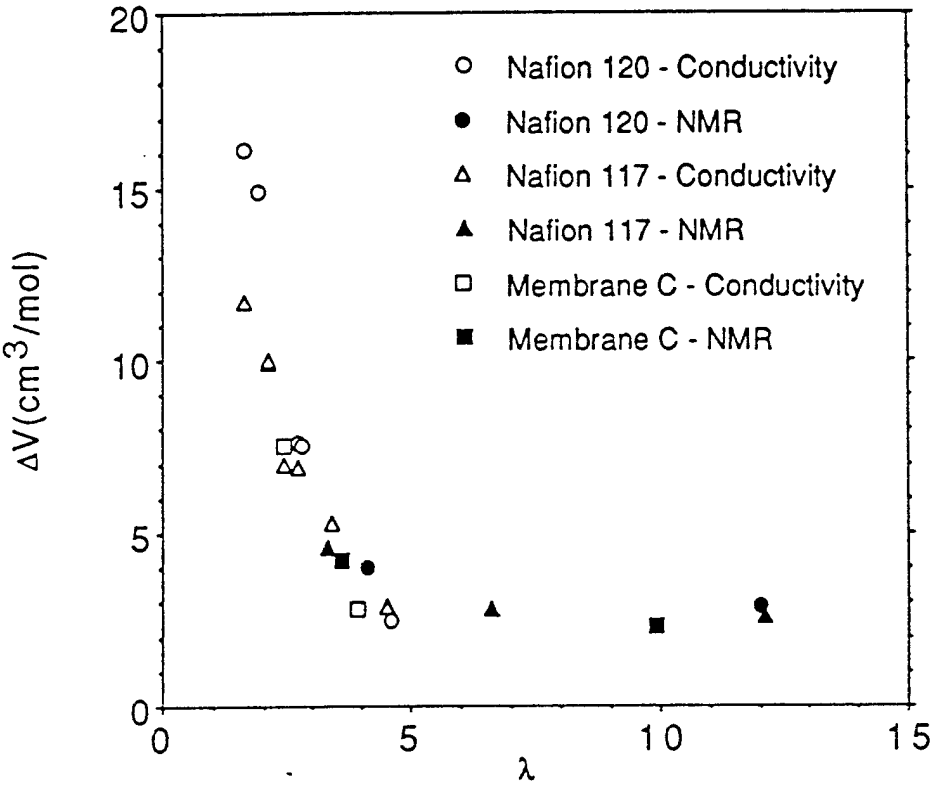
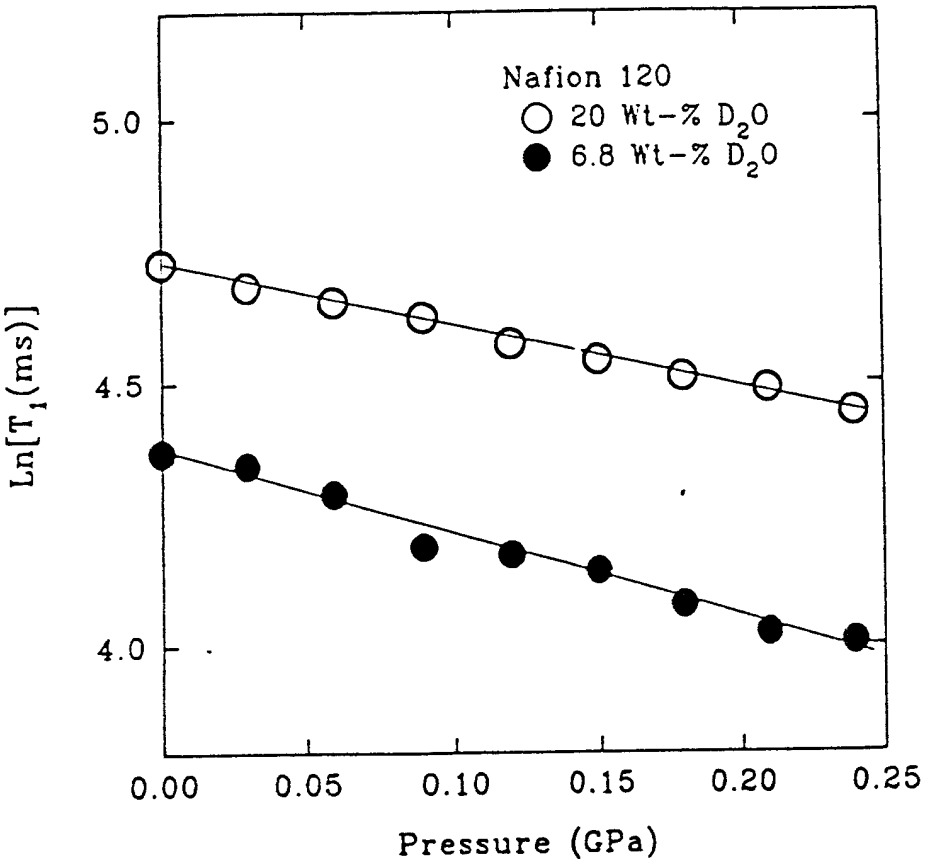

20
15
10
5
0
0
5
10
15
λ
ΔV(cm3/mol)
Nafion 120 - Conductivity
Nafion 120 - NMR
Nafion 117 - Conductivity
Nafion 117 - NMR
Membrane C - Conductivity
Membrane C - NMR

Figure 8


Nafion 120
20 Wt-% D_2O
6.8 Wt-% D_2O
5.0
4.5
4.0
Ln[T_1(ms)]
0.00
0.05
0.10
0.15
0.20
0.25
Pressure (GPa)

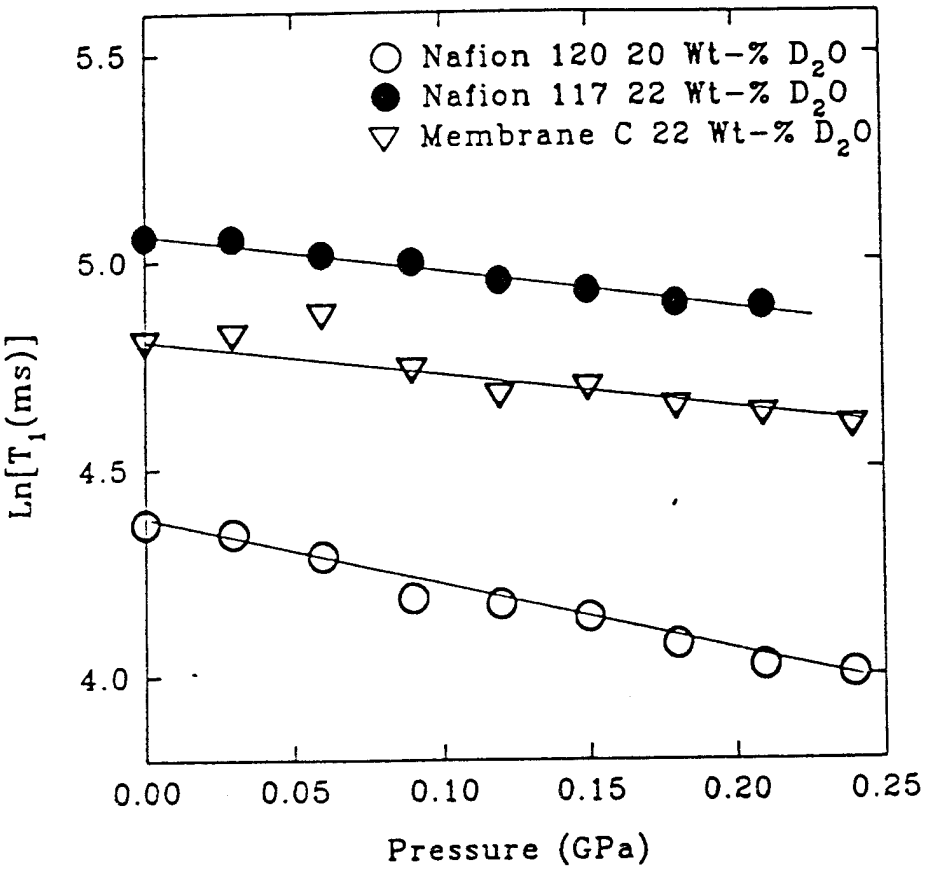

Nafion 120 20 Wt-% D_2O
Nafion 117 22 Wt-% D_2O
Membrane C 22 Wt-% D_2O
5.5
5.0
4.5
4.0
Ln[T_1(ms)]
0.00
0.05
0.10
0.15
0.20
0.25
Pressure (GPa)

Fig. 10